AS91389 vs1 (3 Credits)
Chemical Processes in the world around us

3.3

This achievement standard involves demonstrating understanding of chemical processes in the world around us.

Achievement Criteria

Achievement	Achievement with Merit	Achievement with Excellence
• Demonstrate understanding of chemical processes in the world around us.	• Demonstrate in-depth understanding of chemical processes in the world around us.	• Demonstrate comprehensive understanding of chemical processes in the world around us.

Demonstrate understanding involves processing and interpreting given information to identify, describe, and give an account of chemical processes occurring in the natural world or developed in response to an issue or need. The account given must be supported by the use of chemistry vocabulary, symbols, conventions, and equations.

Demonstrate in-depth understanding involves making and explaining links between chemical processes, and the consequences of the chemical processes for the environment or people. This requires explanations that integrate chemistry vocabulary, symbols, conventions, and equations.

Demonstrate comprehensive understanding involves an evaluation of the impact of, and issues that have arisen from, the chemical processes. This involves elaborating on, comparing and contrasting, or analysing the links between the chemical processes and their consequences. This requires the consistent integration of chemistry vocabulary, symbols, conventions, and equations.

Introduction

A company wishes to mine gold in a small community. The process the company plans to use to extract the gold involves using cyanide. This assessment activity requires you to prepare a report for the local council that outlines the chemical processes involved and the effect on the environment of this extraction method.

You will be assessed on the comprehensiveness of your report and on your evaluation of the impact of, and issues that have arisen from, chemical processes.

You have one week of in-class time to review and add to the chemical data provided, then one week to prepare the report in your own time.

NO EXTENSION WILL BE GRANTED WITHOUT A MEDICAL CERTIFICATE

Task

Write a report that demonstrates an understanding of the processes involved in the extraction of gold from ore using cyanide and the environmental issues involved with the chemical processes.

You will be assessed on how well your report demonstrates your understanding of the chemical processes involved in the extraction of gold using cyanide and the environmental effects of these processes.

In your report:

Include appropriate chemical equations to illustrate the chemical processes occurring.

Elaborate on the steps involved in the chemical processes.

Identify and explain how the chemical processes are linked to environmental effects.

Compare and contrast the chemical processes used to reduce environmental effects of the cyanide extraction processes.

Useful Sites:

International Cyanide Management Code for the gold mining industry. Cyanide Facts: www.cyanidecode.org/cyanidefacts.php

Martha Mine, Waihi, New Zealand: http://www.marthamine.co.nz

Cyanide Remediation: Current and past technologies: www.engg.ksu.edu/hrsc/95Proceed/young.pdf

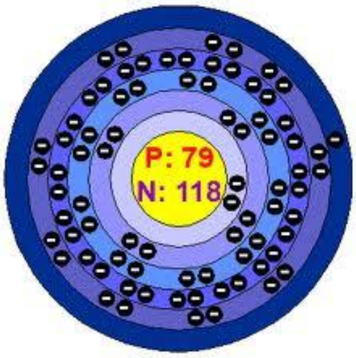
Best practice Environmental Management in Mining: www.ret.gov.au/resources/Documents/LPSDP/BPEMCyanide.pdf

Cyanide – The Facts: www.geology.gov.yk.ca/pdf/MPERG 2001 2.pdf

www.newmontwaihigold.wikispaces.com

Gold – The Chemistry

Gold is a transition metal element in row 6 of the periodic table.



Atomic number 79
Atomic mass 196.9655 $g.mol^{-1}$
Pauling Electronegativity 2.4
Density 19.3 g.cm-3 at 20°C
Melting point 1062 °C
Boiling point 2000 °C
Van der Waals radius 0.144 nm
Ionic radius 0.137 nm (+1)
Electronic configuration [Xe] $4f^{14}$ $5d^{10}$ $6s^{1}$
1st ionisation energy 888 $kJ.mol^{-1}$
2nd ionisation energy 1974.6 $kJ.mol^{-1}$
Reduction potential +1,68 V (Au+/ Au)
Discovered c.a. 3000 BC

Gold is at the "bottom" of group 11, and shows many similarities with both Cu and Ag which are also in group 11.

Gold is known for its lack of reactivity – this is due to its lattice structure and reluctance to form bonds (think about bond energies).

It forms positive ions like other metals.

It is a coloured transition metal due to d-orbital shifts.

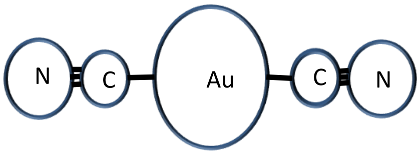
Note that the d-orbital has filled at the expense of a partially filled 6s orbital (remember 6s should fill and empty first Cf. Cu); this means that gold can either lose or accept an electron, forming:

Au^{+} and Au^{-} - this is **NOT** typical of metals – Cu does not do this.

Gold has the highest reduction potential of all metals and can accept electrons from other metals. It has the oxidation states –1, 1, 2, 3, 4, 5.

Compounds containing the Au^{-} anion are called aurides. Caesium auride, CsAu Rubidium auride RbAu and Potassium auride KAu are the commonest.

The normal oxidation states of gold include +1 gold (I) (aurous) compounds and +3 gold (III) or auric compounds.
Au(I) compounds are typically linear. A good example is $Au(CN)_2^-$, which is the soluble form of gold encountered in mining.



Gold(III) is a common oxidation state as in gold(III) chloride, $AuCl_3$.

Most of the other oxidation states are formed in complex ions (Cf. AS2.2)

Some gold compounds exhibit **aurophilic bonding**, which describes the tendency of gold ions to interact at distances that are too long to be a conventional Au-Au bond but shorter that van der Waals bonding. The interaction is estimated to be comparable in strength to that of a hydrogen bond – these “extra bonds” give greater lattice stability.

Mixed valence compounds (Cf. Fe_3O_4)

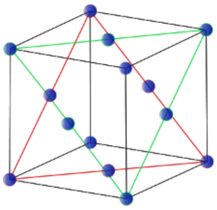
Some compounds have mixed oxidation states, in these gold has an intermediate oxidation state. e.g. "AuS" features equal amounts of Au(I) and Au(III) – NOT Au(II).

Physical Properties

Gold behaves as a typical metal:

It is a solid at room temperature with a high melting and boiling point.

It forms metallic lattices:



The lattice is metallic bonded and contains **ATOMS** with mobile valence electrons.

It is an excellent conductor of electricity and is used in electronic circuitry.

It is highly lustrous (shiny) which makes it a good reflector as well as a good conductor of heat.

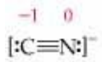
It is the most malleable metal and can form foil layers just a few atoms thick – hence its use in Rutherford's Experiments.

It is the most ductile metal, forming wires thinner than a human hair.

Visit http://www.gold.org/technology/uses/interactive_town/ for uses of gold.

Cyanide – The Chemistry

Cyanide is an anion: $C \equiv N^-$.

Lewis Structure: 

It is the conjugate base of the weak acid HCN (hydrocyanic or prussic acid).

$HCN + H_2O \leftrightharpoons H_3O^+ + CN^-$

It acts as a ligand for many transition metals including gold.

The CN^- ion is a pseudohalide which means it behaves like F^-, Cl^-, Br^- or I^-.
It is also isoelectronic with >CO (carbonyl), so metal carbonyls and cyanide complexes have a similar structure.

The extreme toxicity of CN^- is due to its irreversible formation of a complex with Fe^{2+} and Fe^{3+}. This prevents oxygen uptake in the lungs.

The ability of CN^- to form very stable complexes with silver ($Ag(CN)_2^-$) and gold ($Au(CN)_2^-$) is the basis for its use in the extraction and purification of these metals.

When forming a single metal-ligand bond (monodentate ligand) it is the carbon atom that bonds, but when it bonds at both ends (didentate ligand),both the C and N bond to metals to form infinite linear (chain) polymers as in AgCN, AuCN, $Zn(CN)_2$, and $Cd(CN)_2$.

Cyanide in the Environment

Cyanide is produced naturally in the environment by various bacteria, algae, fungi and numerous species of plants including beans (coffee, chickpeas and lima), fruits (seeds and pits of apple, cherry, pear, apricot, peach and plum), almond and cashew nuts, vegetables of the cabbage family, grains (alfalfa, and sorghum), roots (cassava, potato, radish and turnip), white clover and young bamboo shoots.

Incomplete combustion during forest fires is believed to be a major environmental source of cyanide, and incomplete combustion of articles containing nylon produces cyanide through depolymerization.

Once released in the environment, cyanide is very reactive:

Complexing:
Cyanide forms ionic complexes with many metals. Most cyanide complexes are much less toxic than cyanide, but some are not very stable.
Weak acid dissociable complexes such as those of copper and zinc are unstable and release cyanide back to the environment.

Iron cyanide complexes are especially important due to the large amount of iron in the soil, and the extreme stability of this complex under most environmental conditions. Iron cyanides **do decompose in ultraviolet light** and this could be an issue where there are large concentrations "under the ozone hole". Although if there is enough ultraviolet light to decompose Iron Cyanides then it will also decompose free cyanide to carbon and nitrogen

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Precipitation:
Iron cyanide complexes form insoluble precipitates with iron, copper, nickel, manganese, lead, zinc, cadmium, tin and silver over a pH range of 2-11.

Adsorption:
Cyanide and cyanide-metal complexes are adsorbed on organic and inorganic constituents in soil, including oxides of aluminium, iron and manganese, certain types of clays, feldspars and organic carbon. Although the strength of cyanide retention on inorganic materials is ~~unclear~~variable, cyanide binds very strongly to organic matter. The fact that the gold cyanide complex adsorbs onto activated carbon is very important for economic gold extraction. ~~(hence the use of activated carbon in the extraction of gold).~~

Oxidation:
Cyanide oxidizes to the less toxic cyanate with strong oxidizing agent such as ozone, hydrogen peroxide, Caro's Acid (mixture of sulphuric acid and hydrogen peroxide) or hypochlorite.

Oxidation with peroxide:

$$H_2O_2 \xrightarrow{hv} 2OH\cdot$$

(OH· Is a free radicle and very reactive – it has an odd electron).

Comment [DB1]: Has the spelling of radical changed since all the years I went to school?

$CN^- + 2OH\cdot \rightarrow CNO^- + H_2O$

The cyanate is an intermediate product. In the second step cyanate is further oxidised to carbon dioxide (which ultimately forms bicarbonate) and nitrogen gas:

$CNO^- + 3OH\cdot \rightarrow HCO_3^- + \frac{1}{2}N_2(g) + H_2O$

Adsorption of cyanide on both organic and inorganic materials in the soil seems to promote its oxidation under **natural** conditions.

Gold and Cyanide

The MacArthur-Forrest process is a method for extracting gold from low-grade ore by converting the gold to a water soluble cyanide complex.

It is the most commonly used process for gold extraction. But only represents about 13% of cyanide used globally, the rest being used to manufacture plastics, adhesives, and pesticides.

The process is controversial because cyanide is so toxic to living organisms. Cyanide has been used to extract precious metals from crushed rock for more than 100 years. Modern recovery methods that utilise cyanide in water-based solution can recover nearly 100% of the contained precious metals (i.e. gold and silver), making it profitable for mining companies to process low-grade ores.

The chemical reaction used is called the Elsner Reaction:

$4Au + 8NaCN + O_2 + 2H_2O \rightarrow 4NaAu(CN)_2 + 4NaOH$

The Waihi Process:

Rock is blasted into movable sized lumps.

Rock is crushed and mixed with lime (calcium oxide) and water and large steel balls (mechanical grinding in a grinding ~~ball~~ mill the outside and inside are shown below).

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Sodium cyanide and oxygen is added to the slurry in leach tanks.

The pH in these tanks is about 10 – 11 keep the cyanide soluble so that it does not form hydrogen cyanide gas which could escape into the atmosphere.

The oxygen is necessary for the required reaction to take place:

$4Au + 8NaCN + O_2 + 2H_2O \rightarrow 4NaAu(CN)_2 + 4NaOH$
(Elsner's equation)

The gold, silver and a small amount of copper is complexed with the cyanide ligands. This makes them soluble in water.

The slurry then flows to adsorption tanks which contain screens of activated carbon. The activated carbon then adsorbs the gold and silver complexes onto the activated carbon screens. During this process, the carbon flows counter current to the slurry to ensure maximum adsorption. This is done by screens which allow the slurry to pass but the carbon is kept in the tank, a portion of the slurry (containing carbon) in the tank is passed to the previous tank in the sequence, the slurry then goes through the screen in the tank and returns to the tank it originally came from but the carbon is now in the "new tank" which is upstream from the slurry flow.

The carbon removes the gold and silver from the slurry making it barren the photos below show the adsorption circuit and the carbon removed from the slurry.

The barren slurry which contains very little cyanide (100 ppm CN is reduced to 5-10 ppm in the tailings dam supernatant liquid- the discharge requirement is less than 0.1ppm which is achieved using a cyanide destruct circuit~~) is then treated and then transported to the waste rock embankment~~. Using UV and bacteria and other natural means any remaining cyanide is quickly broken down:

A large number of plant species (~2,000) as well as some fungi and bacteria can synthesize enzymes to break down cyanide. They then absorb the ammonia made. *Pseudomonas fluorescens* can grow in cyanide concentrations ≤300 μM (micromoles or 10^{-6} moles)

$$HCN + O_2 + 2NADH + 2H^+ \rightarrow [HCONH_2] + H_2O + 2NAD^+$$

$$[HCONH_2] + H_2O \rightarrow HCO_2H + NH_3$$

$$HCO_2H + NAD^+ \rightarrow CO_2 + NADH + H^+$$

$$\text{Sum}: HCN + O_2 + NADH + H^+ \rightarrow CO_2 + NH_3 + NAD^+$$

Biologists will recognise NAD and NADH, if you are not a biology student, just accept that it is a redox agent present in living cells.

The activated carbon is pulled out on screens with the gold and silver complexes attached. The screens carbon isare washed or eluted: first with acid to remove carbonate which can block the Au/CN complex and then with hot water to remove the Au/CN complex (125° C and 2.5 b).

The electrowinning process takes the gold from the cyanide complex. It is a form of electrolysis with stainless steel electrodes: mesh for the cathodes and punch plates for the anodes.

During the electrolytic process oxygen is released at the anode whilst at the cathode a combination of hydrogen evolution and gold deposition occurs:

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^- \text{ anode}$$
$$2e^- + 2H_2O \rightarrow H_2 + 2OH^- \text{ cathode}$$
$$e^- + Au(CN)_2^- \rightarrow Au + 2CN^- \text{ cathode}$$

The gold and silver deposit on the cathode. The cathodes are water blasted to remove the metals. The sludge from this washing process is dried and smelted with a mixture of boric acid, silica, sodium nitrate and sodium carbonate.

This produces a borosilicate glass which adsorbs any contaminant metals e.g. Fe Cu and some of the Ag – this glass is sent back into the mill for grinding.

From the smelt Doré bars are formed which are a mixture of Au and Ag. These bars are sent to Perth in Australia where a specialised plant separates the gold from the silver.

The carbon is heated to 700°c in steam (so that is does not burn) and recycled.

Any ~~waste slurry~~excess water on the tailings dam- is treated at the water treatment plant, Waihi recives an average of over 2000mm of rain a year which equates to 1,000,000m3 of rain water on to the tailings dam in rainfall. This oxidises any remaining CN with peroxide (see previous section), and the water is then treated with carbon dioxide to lower the pH after removal of the cyanide to bring it to dischargeable standards.

Summary Questions:

1 Have I explained the process of gold extraction?

2 Have I included equations?

3 Have I explained the reactions in terms of electron transfer and thermodynamics?

4 Have I included equations?

5 Have I reviewed ALL the environmental issues associated with the process (not just the main one)?

6 Have I included equations?

7 Have I adequately explained how such issues can be dealt with?

8 Have I included equations?

9 Have I explained why gold is in such demand (all uses not just jewellery)?

10 Have I included any community and/or environmental benefits?

11 Have I included responses to likely community concerns?

12 Have I completed the task and not given a review of Waihi processes?

13 You guessed it – have I included equations!